

Composition of Powders Produced by Electrospark Dispersion of Metal Granules in Water

S P Zhuravkov¹, G L Lobanova¹, A V Pustovalov¹, P E Slyadnikov² and L V Nadeina³

¹Institute of High Technology Physics, National Research Tomsk Polytechnic University, 2A, Lenin Ave, Bld. 11, 634028, Tomsk, Russia

²The faculty of innovative technologies, National Research Tomsk State University, 36, Lenin Ave, 634050, Tomsk, Russia

³Institute of Natural Resources, National Research Tomsk Polytechnic University, 2A, Lenin Ave, Bld. 5, 634028, Tomsk, Russia

E-mail: zhursp@yandex.ru

Abstract. The results of experimental studies of metal powders composition produced by electrospark dispersion according to the scheme “metal electrodes – metal granule loading – distilled water” are given in the paper. With a help of X-ray diffraction analysis and other methods, it was found that chemical and phase composition of dispersion products is determined by affinity of metal to oxygen.

1. Introduction

Metal powders, used in different technological processes, must possess not only intended sizes of particles, but also, according to chemical composition and properties, they must comply with specific metal or alloy. The investigations of physico-chemical processes, developing under conditions of metal powder production by various methods, are relevant today.

The method of metals dispersion by electric spark was offered by B.R. Lazarenko and N.I. Lazarenko [1]. The method is that the granules of metal are poured between two electrodes in the power fluid bath (water or organic liquid), and then voltage impulses with a given amplitude value apply to the electrodes, and spark discharges are carried out between granules of metal. The metal dispersion under these conditions is caused by thermal processes developing in the discharge channel. Microdischarges observed as sparking occur between pairs of metal granules due to the influence of electrical energy impulses. These pairs of metal granules are located in equipotential zones of the interelectrode gap. Due to close gaps between particles involving in the process, base energy given off in discharge channels is used to heat metal in zones of anode and cathode spots, located on these particles surfaces [2]. It causes local heating of metal to melting and boiling temperatures. As a result of it, melting, evaporation and dispersing of molten metal occur. A dimple is formed on the surface of the eroded metal particle. Spherical or tear-drop shapes are characteristic of the electroerosion powder particles of metals, and these shapes verify their liquation nature, i.e. the metal liquid separation from locally heated channel zone of metal granules (Figure 1).



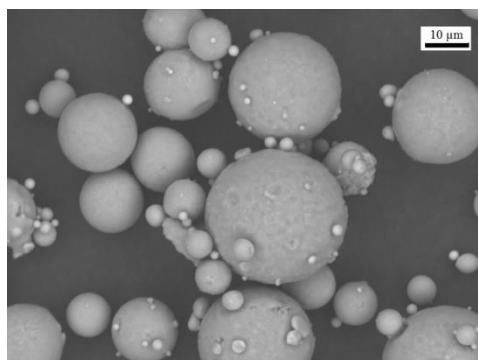


Figure. 1. Products of iron electrospray dispersion in water

The power fluid is also subjected to processes attending development of the discharge channel: dissociation and ionization of fluid occur. There are primary ionized particles of hydrogen and oxygen in the discharge channel in water [3]. Plasma property of the discharge channel is to accumulate energy, and then to use it slowly. These plasma properties lead to the discharge channel degeneration. It degenerates into a steam and gas bubble, in which recombination processes such as $H + H \rightarrow H_2$; $H + \text{wall} \rightarrow (1/2)H_2$; $O + O \rightarrow O_2$ and so on occur after completing processes in the channel [4]. Moreover, water is exposed to hot particles of molten metal spitting from erosion dimples, and gaseous products are formed in accordance with overall reaction $2H_2O + 116 \text{ kcal} \rightarrow 2H_2 + O_2$.

Therefore, hot metal melted by electrical erosion at first interacts with gaseous products of the steam and gas bubble. Then, flowing out into the power fluid, metal interacts with it. If water is used as power fluid, metal cools when it is in the hydrothermal oxidation zone. In consequence of these processes, oxide phases appear in composition of iron, niobium powders produced by electroerosion method [4]. The analysis of existence conditions of metallic and oxide phases of metals at different temperatures and fugitiveness of oxygen is given in the paper [5]. According to degree of affinity between metals and oxygen, the authors divided metals into three groups. Use of these approaches makes the processes be understood easier, so long as development of these processes is possible due to electroerosive production of different metals powders.

The aim of this paper is to study the effect of physicochemical processes on the phase composition of powders, taking into account that these process proceed due to electrospray dispersion of metals such as silver (Ag), zinc (Zn), iron (Fe), titanium (Ti) in water, as well as to obtain basic data to develop an electroerosion technology of the fine powders production with reproducible properties.

2. Experimental

Investigated metals, presenting different groups in accordance with degree of affinity between metals and oxygen [5], are shown in table 1.

Table 1. Classification of metals in conformity with level of oxygen affinity

Group name	Metal
Metals, which can be in equilibrium with non-dissociated water	Ag
Metals, which are unstable in medium containing water, and they corrode. They can exist only in reducing conditions in atmosphere of H_2 and CO	Zn, Fe
Metals, which are stable in special reducing conditions	Ti

The laboratory setup described in the paper [7] was used to produce electroerosion powders of metals. A porcelain jar (1 dm^3) was used as a reactor. Electrodes were made of metal which were in keeping with metal of granulated loading. They were fastened with a help of brackets, and dipped in the jar in the line of the jar's wall to the bottom. Electrode spacing was 60 mm. The interelectrode gap was filled with metal granules at a height of 10-15 mm. Distilled water was used as power fluid;

capacity size 500 cm^3 . After finishing the dispersion stage, the lay of generated suspension was decanted in a receiving container. Electroerosion powders were fractionated with sedimentation or they were settled for thickening. Then they were dried into the vacuum oven, first at temperature no more than 40°C , then they were brought up to constant-weight at 100°C . Produced powders were investigated by the metal component fraction measurement and the phase composition study.

The metal component fraction was determined by method of metal chemical equivalent determination due to oxygen volume displacement and the weight of metal chemical analysis in the sample of powder. The investigation of phase composition and structural parameters of the sample was carried out by X-ray diffraction analysis, with a help of diffractometer Shimadzu XRD-7000 with $\text{CuK}\alpha$ -radiation (Nanocenter, Tomsk polytechnic university). The size analysis of coherent scattering regions (CSR) was carried out with a help of program of full-profile analysis – program POWDERCELL 2.4. The investigation of fine powders morphology was carried out by transmission electron microscopy method (TEM) using the electron microscope JEM-2100 (JEOL) (Nanocenter, Tomsk polytechnic university). The value of produced powders specific surface was determined with the analyzer of specific surface and porosity “Sorptometer M” (CJSC “Katakoni”) according to thermal nitrogen desorption. Due to findings, the software of “Sorptometer M” has calculated value of the investigated samples specific surface by Brunauer-Emmett-Teller method (BET method).

3. Discussion of Results

X-ray patterns of powders produced by electrospark dispersion of investigated metals (Ag, Fe, Zn, Ti) in water are shown in Figures 2,3,6,8.

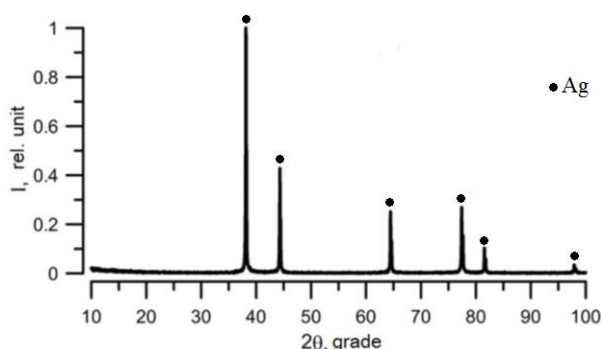


Figure 2. X-Ray diffraction of silver powder

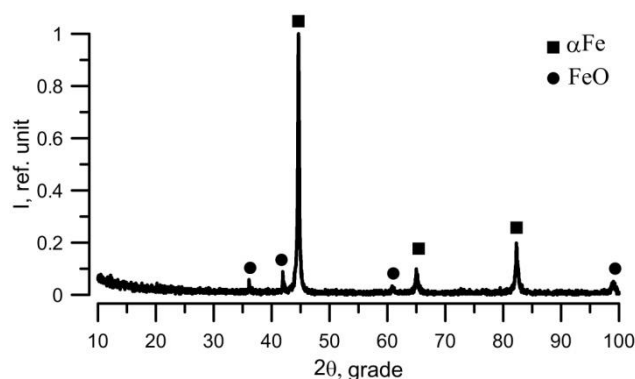


Figure 3. X-ray pattern of iron powder

X-ray pattern of silver powder produced by electrospark dispersion of metallic silver granules in water is shown in Fig. 2. According to data obtained by X-ray diffraction analysis, the product includes well crystallized metallic silver particles; according to phase composition, they are in line with metal of starter granules.

The calculation of crystal lattice parameters of Ag powders was carried out by Rietveld method. It was found that the structure of electroerosion Ag powder corresponds to cubic crystal lattice with near - standard parameters ($a = 4,0871 \text{ \AA}$). Some compounds of silver and water decomposition products (oxygen, hydrogen) were not identified in the produced powder composition.

According to data obtained by X-ray diffraction analysis (Fig. 3,6), in contrast to inert silver, the zinc and iron electroerosion powders are more inclined to oxidation. They contain substances mixture in their composition: not only Fe and Zn metallic phases but compounds of these metals and oxygen.

Having been washed with ethanol and acetone, iron powder dried after electro-impulse dispersion in water consists of two phases, which are in keeping with clear diffraction lines of metallic α -iron (αFe) and iron oxide (II) (FeO) in X-ray pattern (Fig.3). The content of metallic phase of iron in the powder is equal to 85-90%, and the specific surface value of this fraction is no more than $10 \text{ m}^2/\text{g}$.

Physical configuration of fine dispersed fraction particles (according to data obtained by transmission electron microscopy) is presented in Figure. 4.

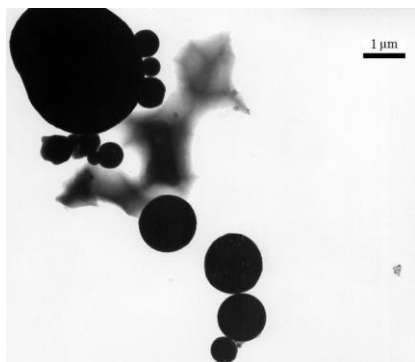


Figure. 4 Transmission electron microscopy of fine dispersed fraction of iron powder

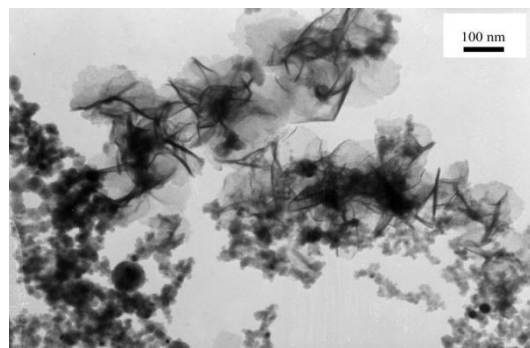


Figure. 5 Transmission electron microscopy of colloidal fraction of iron powder

Electroerosion powders, dried in vacuum oven from aqueous media, contain less metallic iron (60-65%) in their composition. The value of this powder specific surface increases to 40 m²/g due to formation of a new phase (third) – hydroxides. They are formed due to the iron and oxygen interaction in humid atmosphere. Physical configuration of fine dispersed fraction particles is presented in Figure. 5.

X-ray pattern characterizing phase composition of electroerosion powder is given in Figure. 6. Zinc granules were used to produce this powder. According to data, obtained by X-ray diffraction analysis of the selected powder, products of dispersion is a mixture of at least two substances: metallic zinc (Zn) and zinc oxide (ZnO).

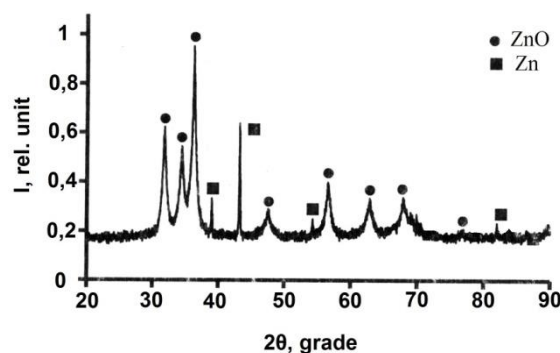


Fig. 6. X-ray pattern of zinc powder

Since high-temperature oxidation processes are such profound ones, so not only metallic zinc finely dispersed particles, produced due to thermal processes in discharge channels (Figure. 7a), but new formations held on their surface (Figure. 7b) are clearly observed in an electronic photography.

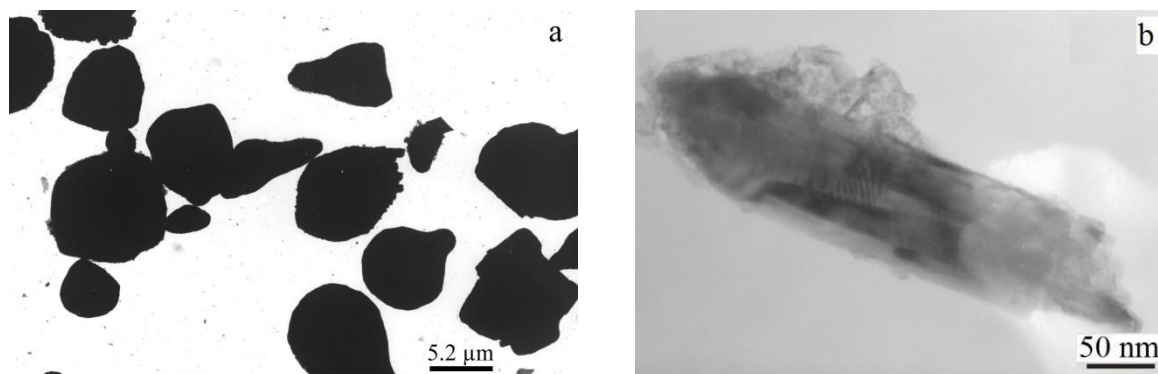


Figure. 7. Electronic photography of powders produced by electrospark dispersion of zinc granules: a) finely dispersed particles, b) single nanorod ZnO

These new formations are presented by eumorphic particles. The particles are long like nanorods, the length of them can be 150 nm or less, and 50 nm or less in cross direction corresponding to red zinc ZnO. The colour of this powder is grey. According to data of chemical analysis, the metallic zinc concentration in powder is no more than 70%.

Even more profound changes in phase and chemical compositions of electroerosion powders can be observed when the titanium electrospark dispersion is carried out. X-ray diffraction analysis data of powder produced from metallic titanium is presented by X-ray pattern in Figure. 8.

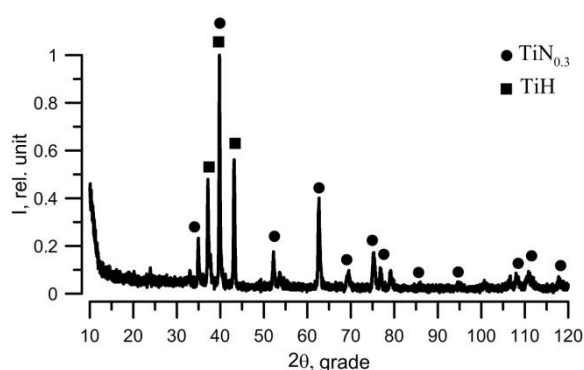


Fig. 8 X-ray pattern of titanium powder

According to data of this X-ray pattern, the lines, which could be classified as pure titanium, are shifted or closed by overlapping of lines which are typical of other substances. It is possible to come to conclusion that there is no pure metallic titanium presence in the powder. Twelve lines, including the most intensive one, are likely can be related to the phase $\text{TiN}_{0.3}$. Three lines can be related to the phase TiH : two independent lines possess the intensity of 68 and 96 %, and the third line is overlapped with the most intensive line of the phase $\text{TiN}_{0.3}$. Some lines can be related to the phase Ti_2O_3 , but nine lines are overlapped with the lines of phase $\text{TiN}_{0.3}$, and only one line is independent.

Therefore, due to data of X-ray diffraction analysis, products of metallic titanium electrospark dispersion in water are likely to be presented as a mixture of at least two phases: $\text{TiN}_{0.3}$ and TiH . Observed behavior of metallic titanium, when in use electrospark dispersion in water, is in agreement with its reported chemical properties and high reactivity, when interacting with nitrogen and oxygen to form titanium nitride and titanium oxide at high temperatures [8].

Moreover, when in use metals electroerosion dispersion, high local temperatures increase sharply the velocity of interaction them with environment. Metals, which are prone to interaction with oxygen

and hydrogen, forming due to water decomposition in a spark, and other gases dissolved in water are able to absorb a great deal of oxygen (and other gases) in short time of the erosion cycle. Adsorbed oxygen can be in metals either in dissolved condition (oxides of the lowest oxidation level) or suboxides, and also endogenous non-metallics can occur. Both the first condition and the second one have an effect on phase composition of the produced metallic powders. The more affinity of original metal to oxygen and other gases in the composition of forming gas atmosphere is, the more effect is. When metallic powders are enriched with oxides, the enrichment has an effect on physical properties, for example, it decreases plasticity. Oxidation-reduction reactions between metals and atmosphere, forming in the process of water (power fluid) decomposition by a spark, are a source of oxygen in metals when in use electroerosion dispersion. When in use electroerosion, interaction of oxygen and metals is complicated by dissolution of oxides in metals, and it decreases their thermodynamic stability a lot.

4. Conclusions

Due to these investigations, it was found that only phase composition of products of the silver electrospark dispersion agrees with phase composition of original metal. The products, including original metal and oxides, are formed from oxygen hungry metals such as zinc and iron under experimental conditions. And the phases, which are in keeping with original metal, are not found in the composition of new products formed from titanium under these experimental conditions.

References

- [1] Lazarenko B R and Lazarenko N I 1964 Author's certificate 70000 USSR. Powder production process and apparatus to produce it. Discoveries Inventions **22** 120
- [2] Goloveyko A G 1966 Izvestiya of higher education establishments. Energy **6** 83-88
- [3] Naugolnyih K A and Roy N A 1971 Electric discharges in water (Moscow: Nauka) 155
- [4] Semkin B V, Usov A F and Kurets V I 1995 Principles of electro-impulse material destruction (St. Petersburg: Nauka) 276
- [5] Asanov U A and Sakavov I E 1967 Izvestiya AS Kirgizskoy SSR **4** 71-75
- [6] Oleynikov B V, Okrugin A V, Tomishin M D et al. 1985 Native metal formation in platform basic rocks (Yakutsk: Nuclear Science SB AS USSR) 188
- [7] Zhuravkov S P, Pustovalov A V, Lobanova G L, Kvashnina O S and Yavorovsky N A 2014 Mechanical Engineering, Automation and Control Systems: Proceedings of International Conference (Tomsk: TPU Publishing House, 16-18 October 2014) 1-4
- [8] Fedotov N P, Alabyishev A F, Rotinyan A P, Vyacheslavov P M, Zhivotinskiy P B and Galnbek A A 1967 Applied electrochemistry (Leningrad: Chemistry) 600